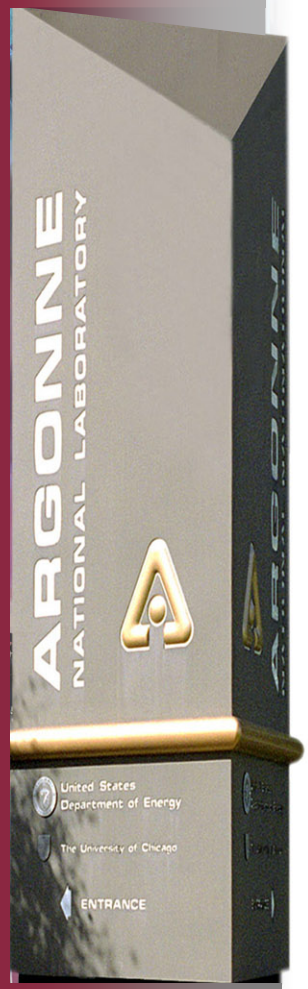
The Cross-cut Review: Science Requiring the Pulsed Structure of the APS X-ray Beam Jan. 26, 2005



Probing Transient Molecular Structures in Photochemical Processes Using Pulsed X-rays

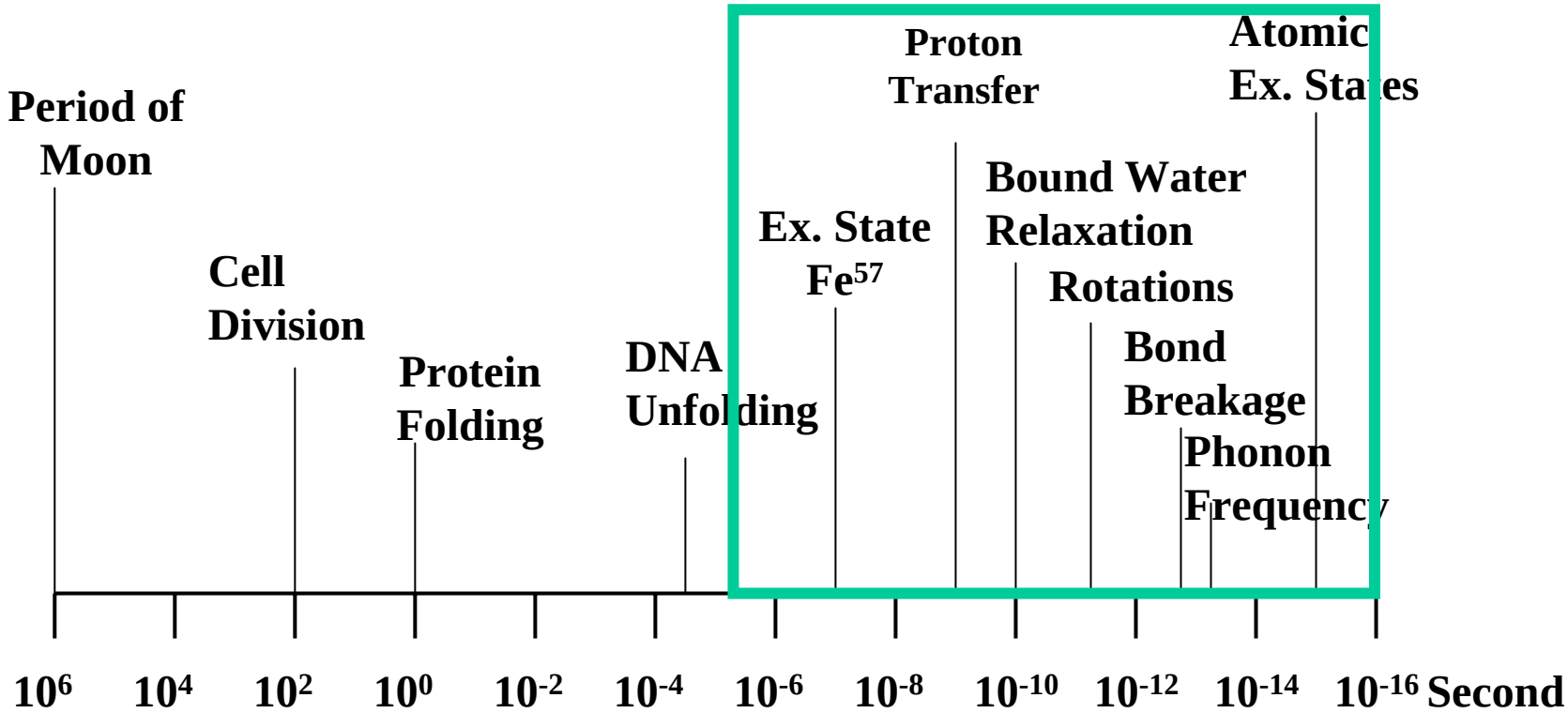
Lin X. Chen David M. Tiede

Chemistry Division
Argonne National Laboratory

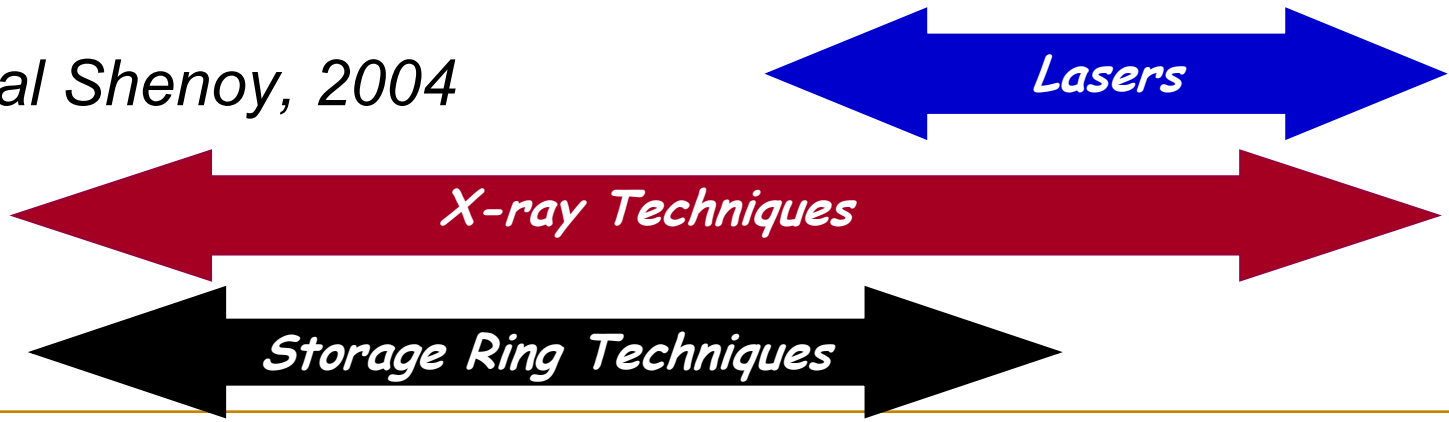
Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Time Domain Science

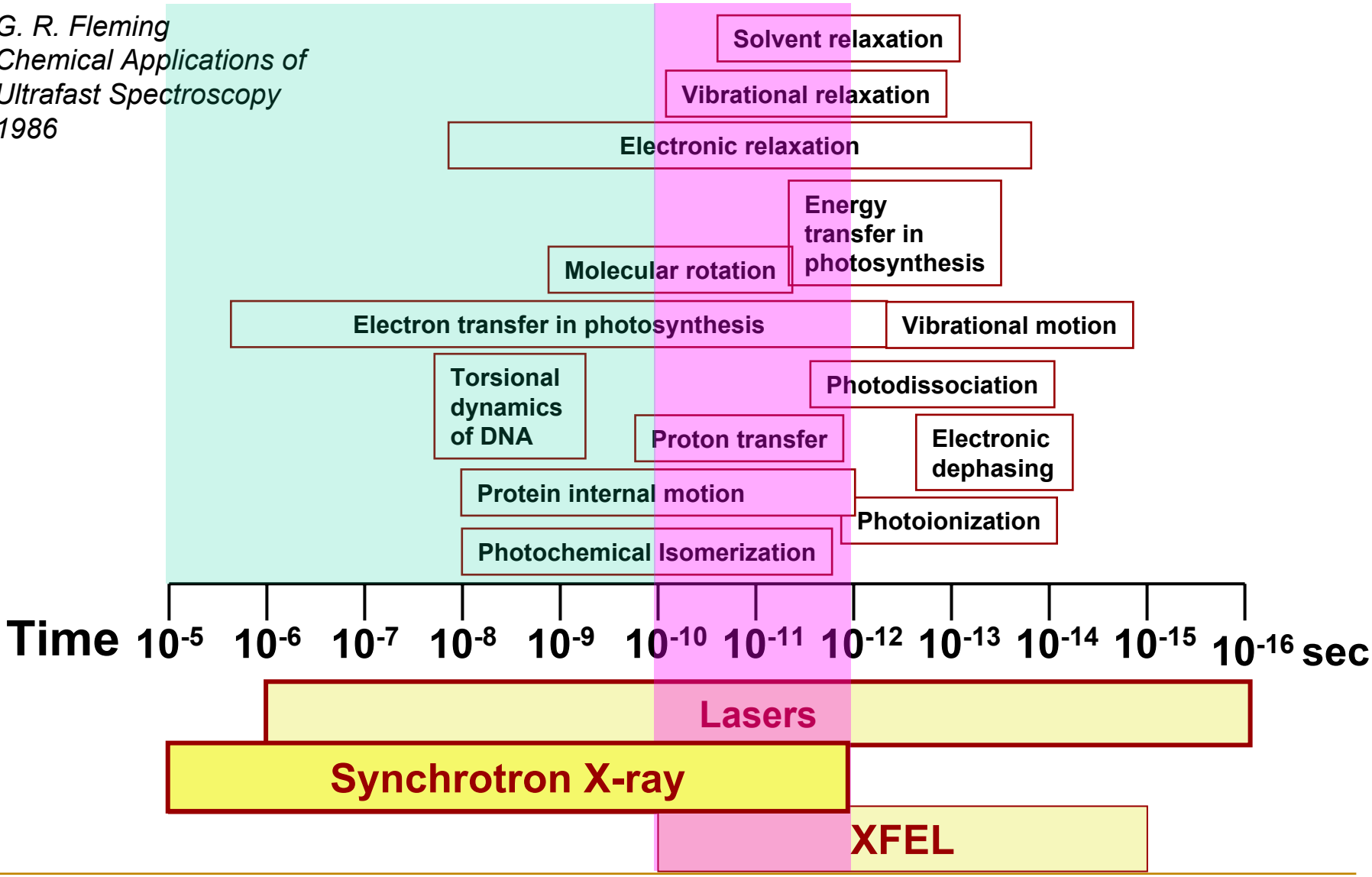


Gopal Shenoy, 2004



Multiple Temporal Scales in Chemical Sciences

G. R. Fleming
Chemical Applications of
Ultrafast Spectroscopy
1986



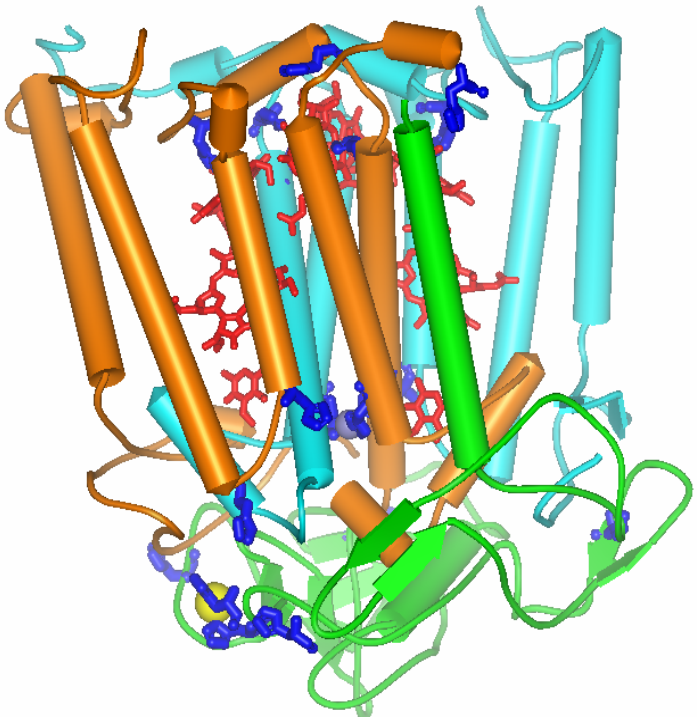
Multiple Length Scales in Chemical Sciences

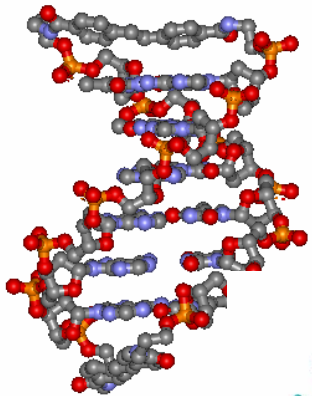
Length

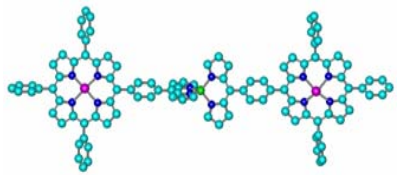
10^4 10^3 10^2 10 10^0 10^{-1} 10^{-2} 10^{-3} Å

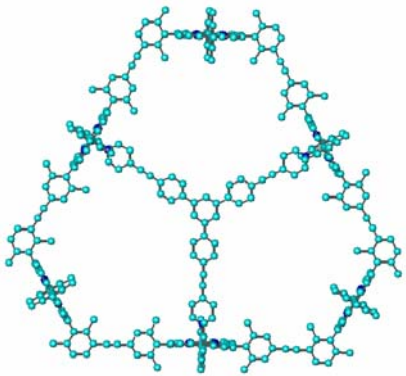
XAFS

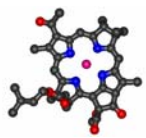
SAXS/WAXS

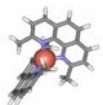






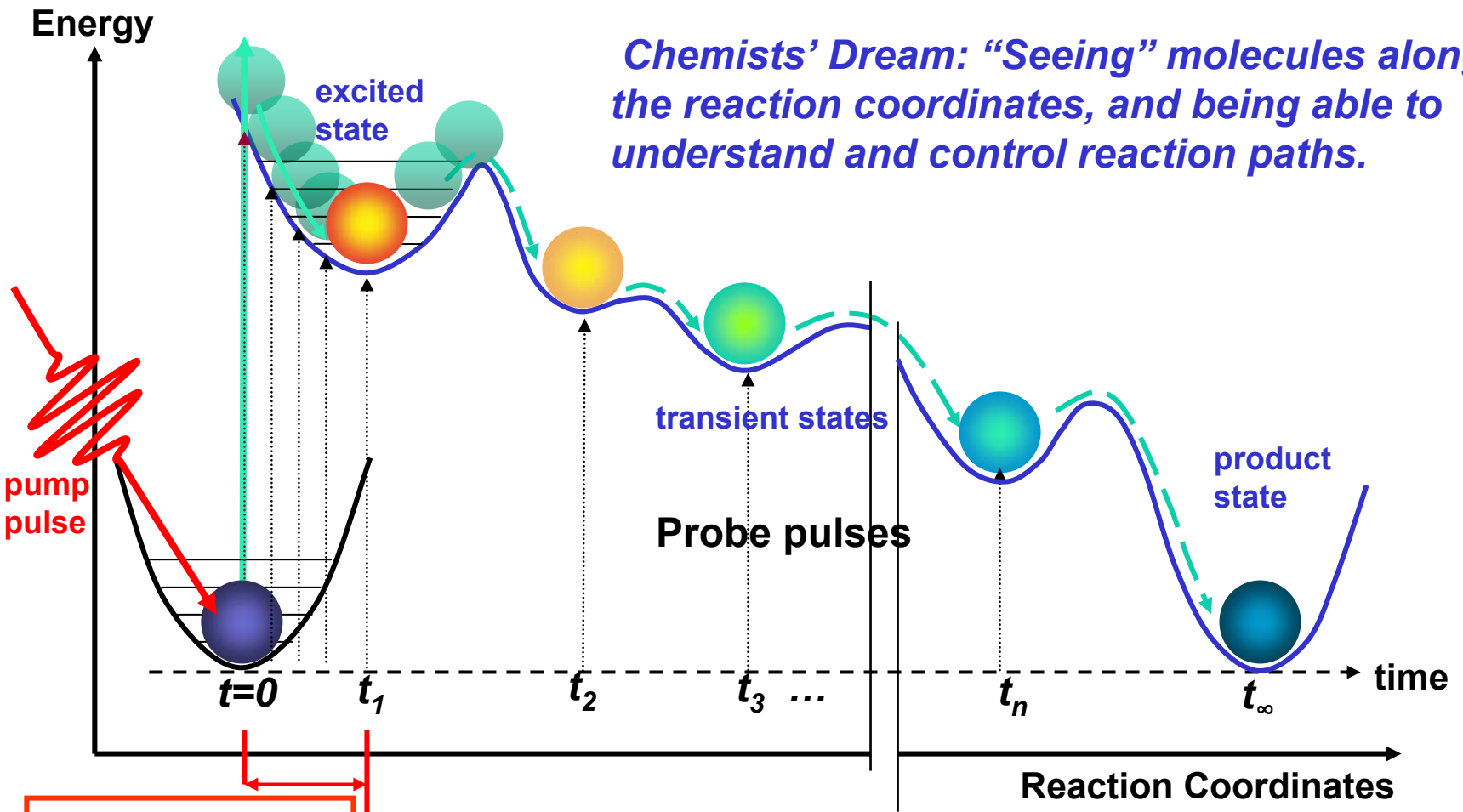






Launching Chemical Processes Synchronously with Laser Pulses

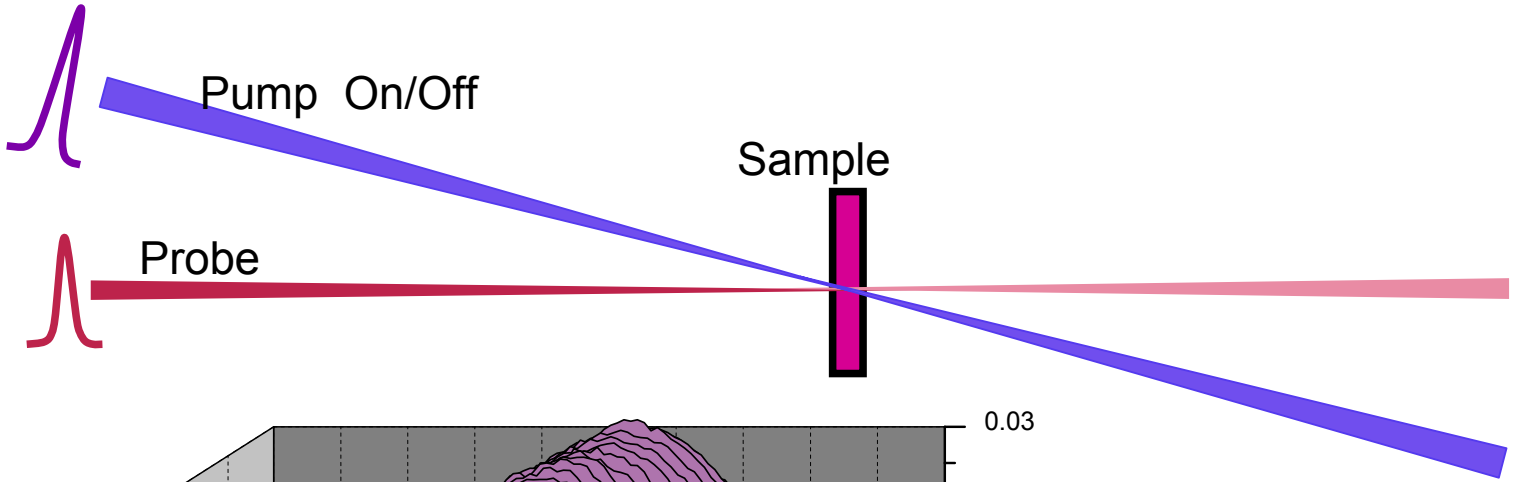
Chemists' Dream: "Seeing" molecules along the reaction coordinates, and being able to understand and control reaction paths.

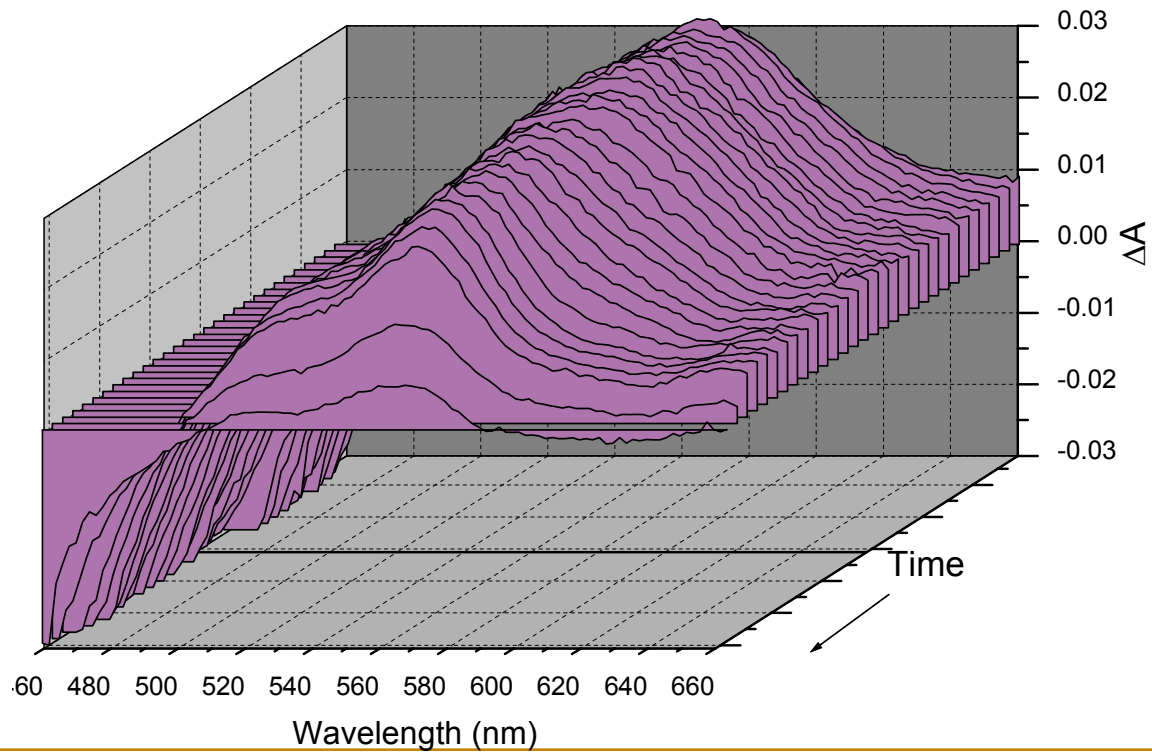


coherent atomic motions on fs to ps time scales → "molecular movie"

incoherent atomic motions leading to discrete thermally equilibrated transient states on ps to s time scales →"molecular snapshots"

Pump-probe Spectroscopy

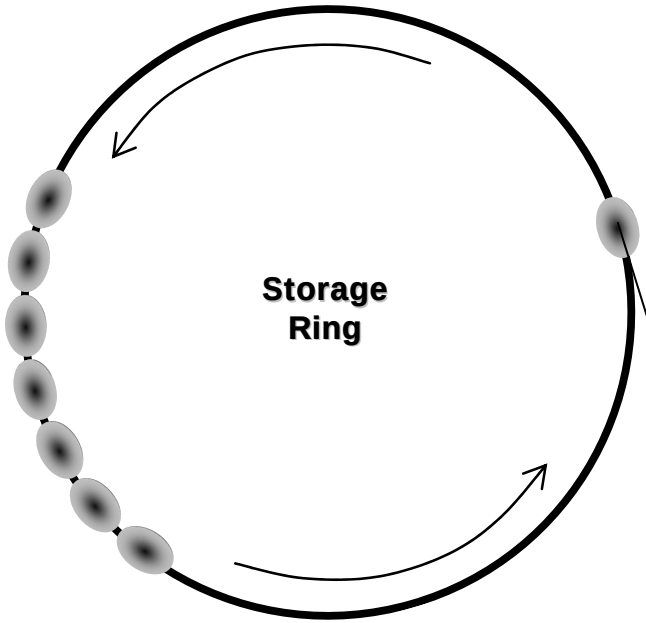


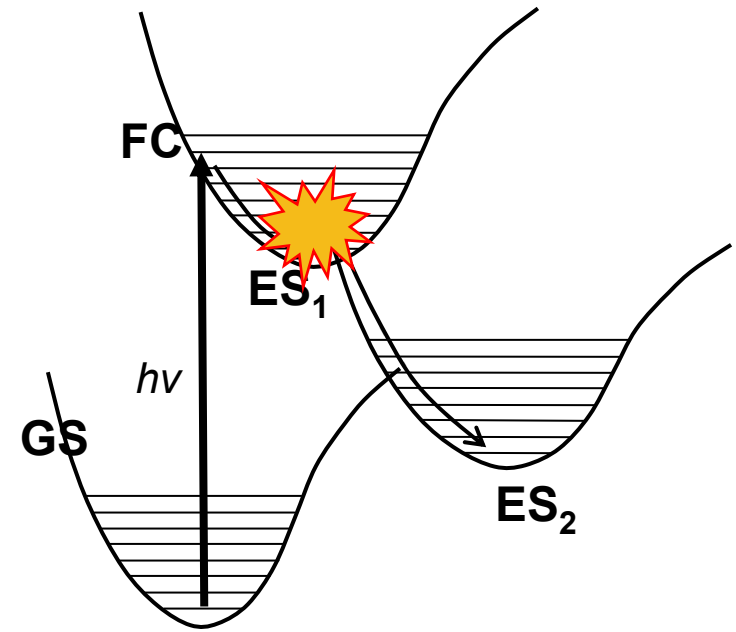


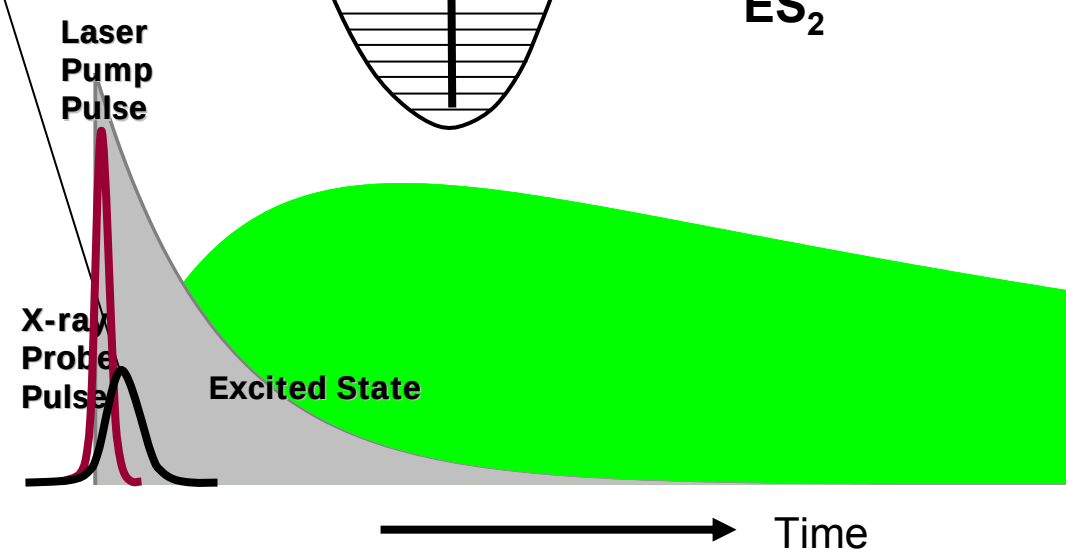
Laser pulse probe: kinetics, energetics coherence

X-ray pulse probe: structures

Capturing Excited State Structures with Pulsed X-rays

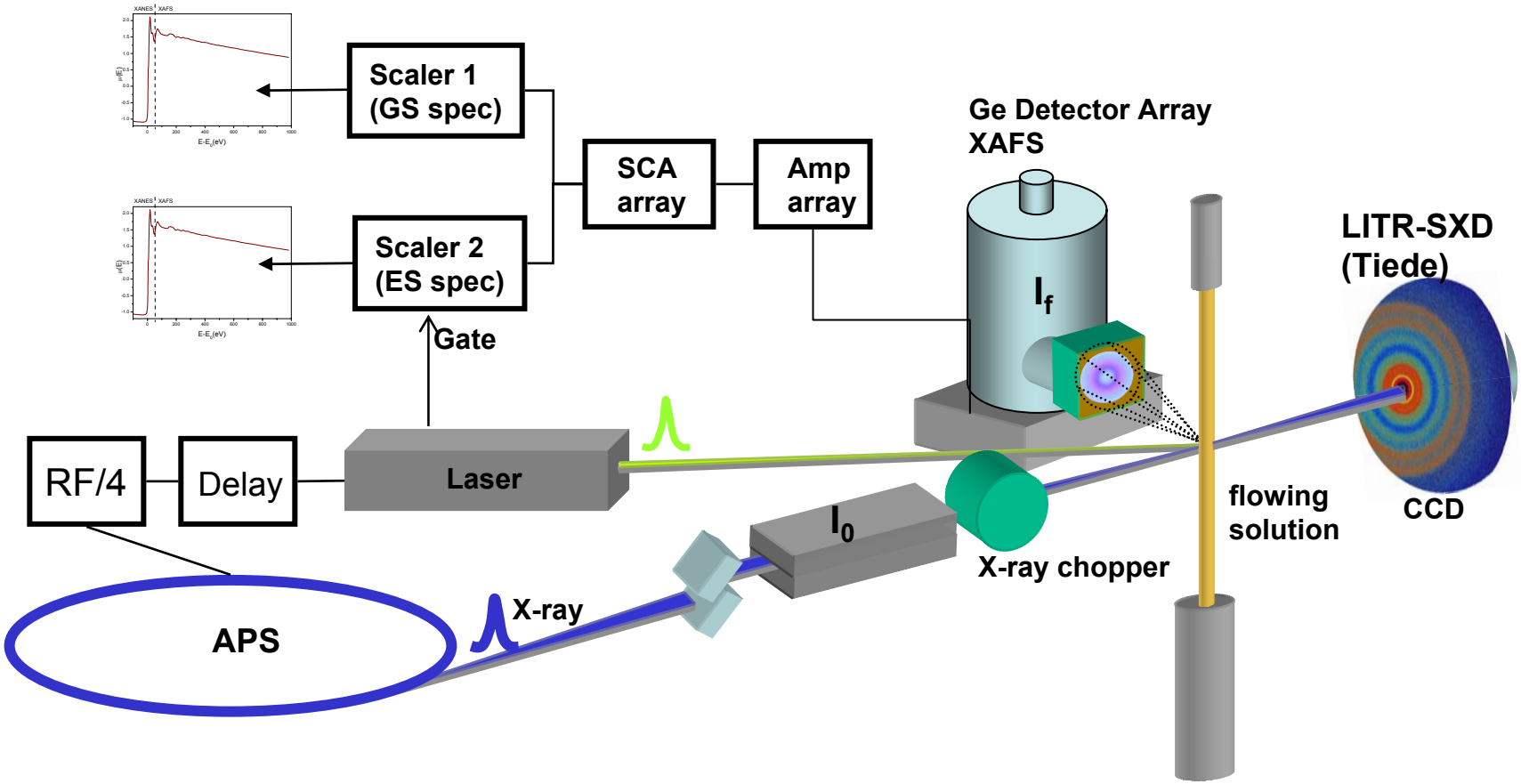




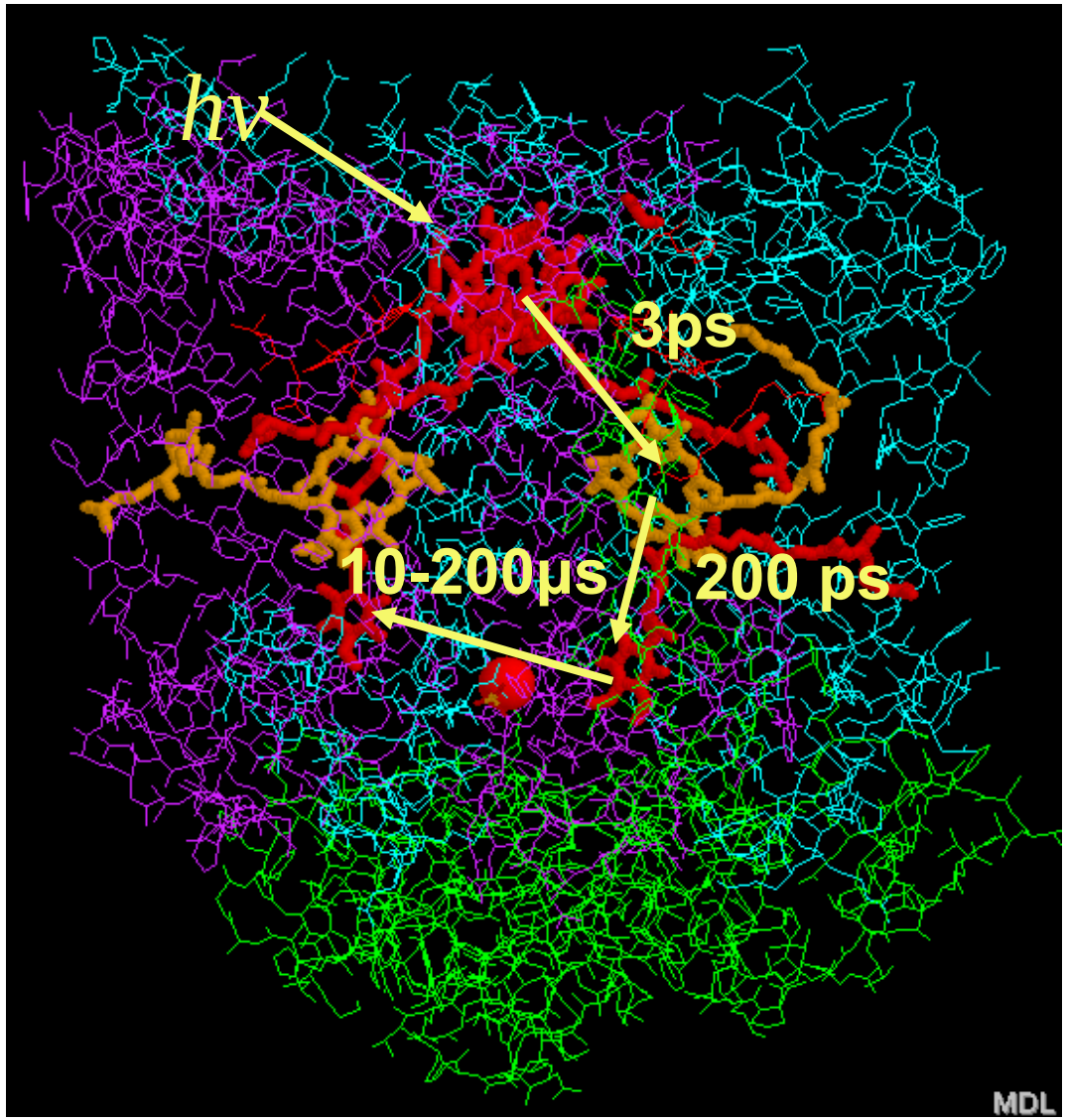


Laser pulse pump
X-ray pulse probe
Intrinsic time resolution:
30 – 100 ps fwhm

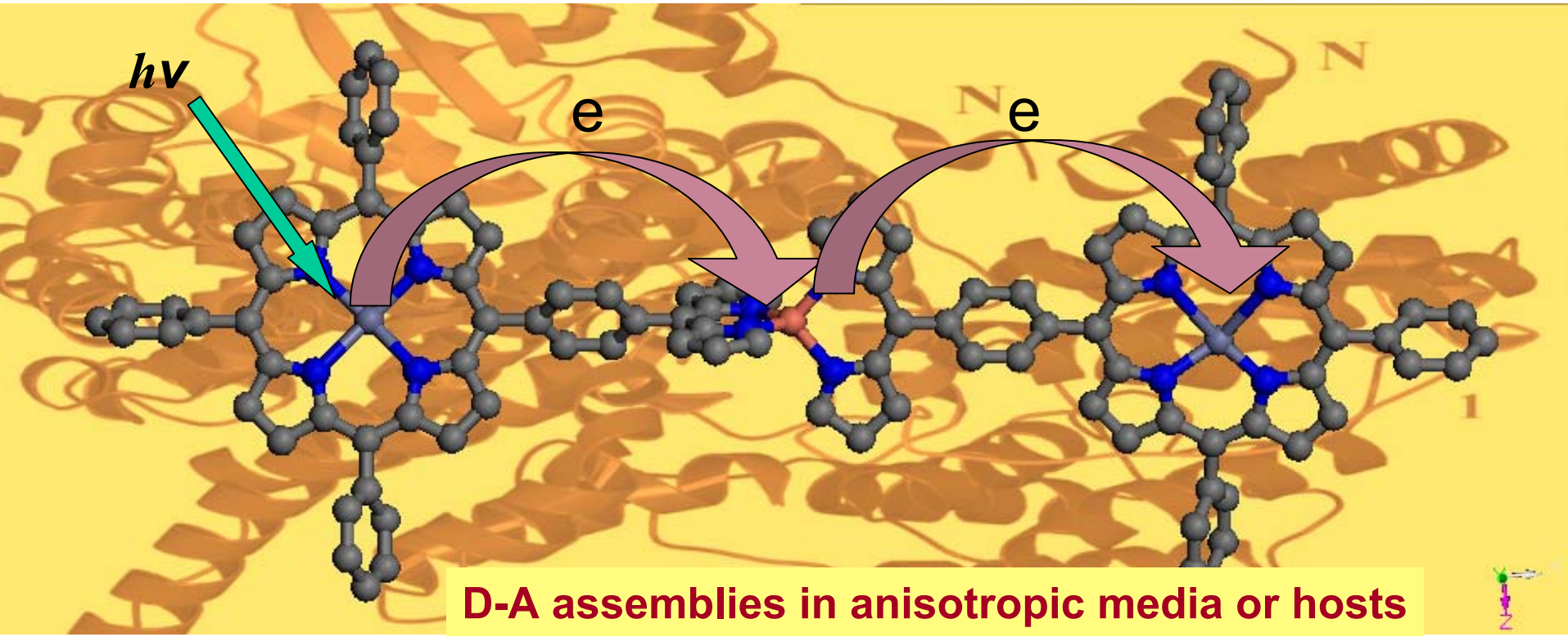
Experimental Setup for Light-induced Time-resolved (LITR-) XAS/WAXS (Beamline 11ID-D)

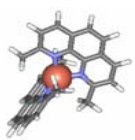
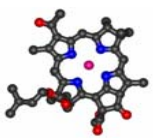
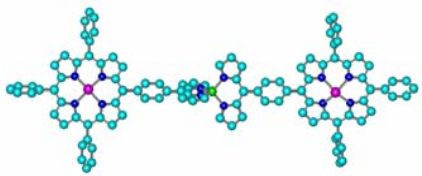
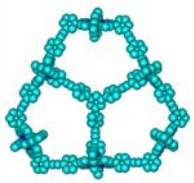
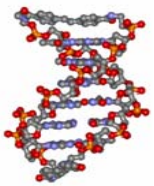
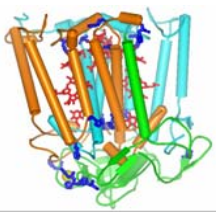


Natural Photosynthesis and Model Systems

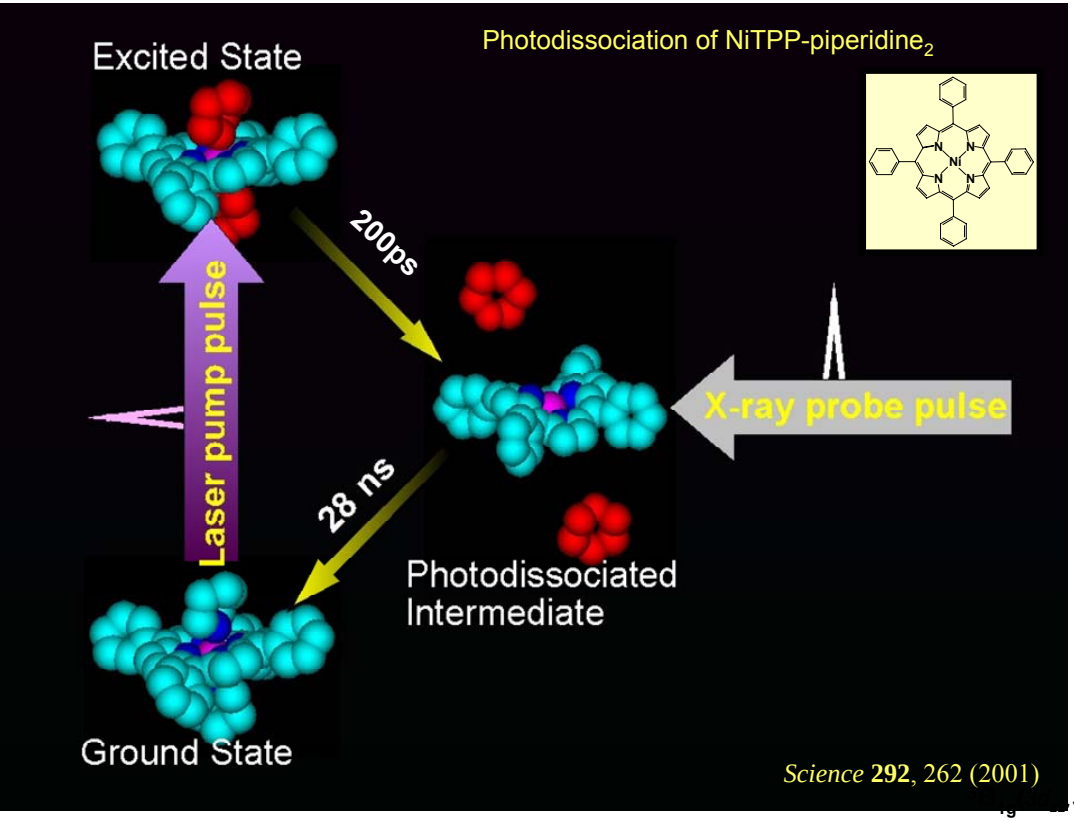


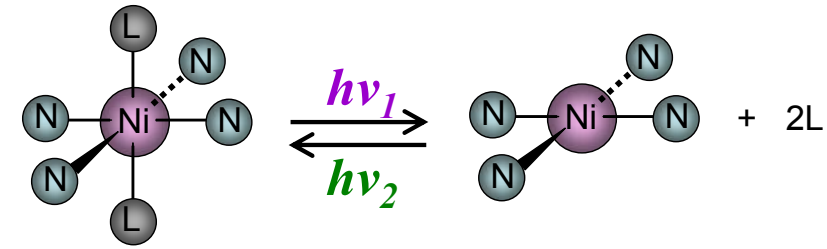
Natural Photosynthesis and Model Systems

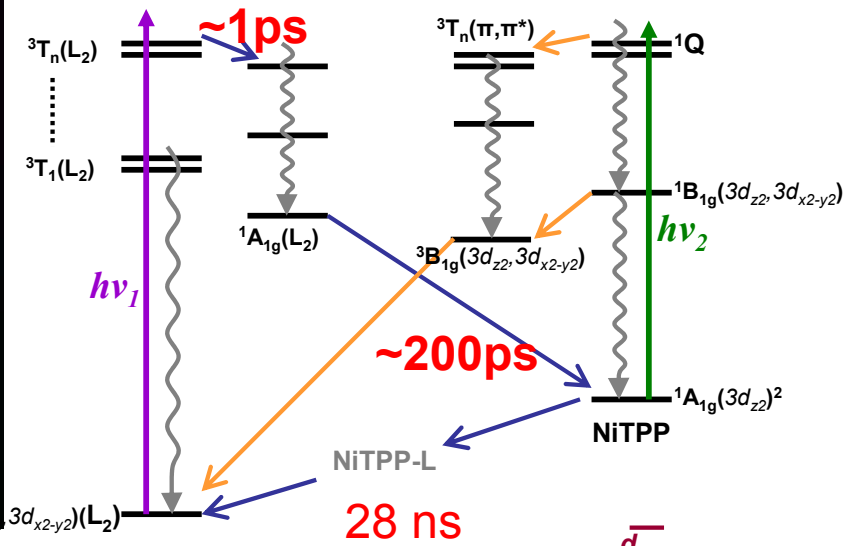


Excited States and Redox Intermediates of Metalloporphyrins and Metallophthalocyanines







- Triplet and single excited state structures;
- Precursor structures before dissociation/association;
- Effects of environment that enhances or hinders ligation/deligation.

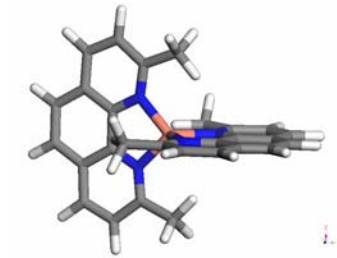
Chen, Jäger, Jennings, Gosztola, Munkholm, Hessler, Science, 292, 262-264(2001).

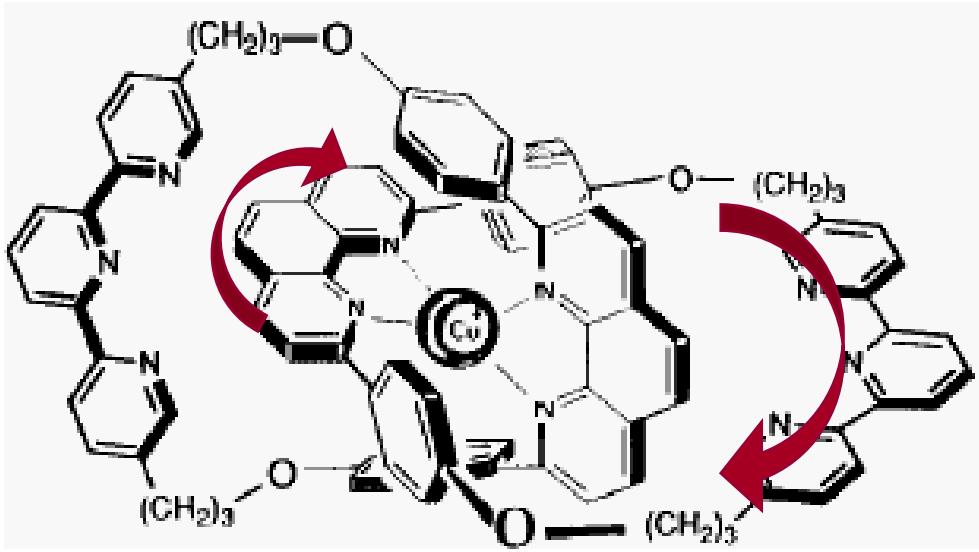
Metal-to-Ligand Charge Transfer (MLCT) Excited State Structures of Transition Metal Complexes

$$[Cu^{I}(dmp)_2]^+ \xrightarrow{h\nu} [Cu^{II}(dmp^-)(dmp)]^+$$

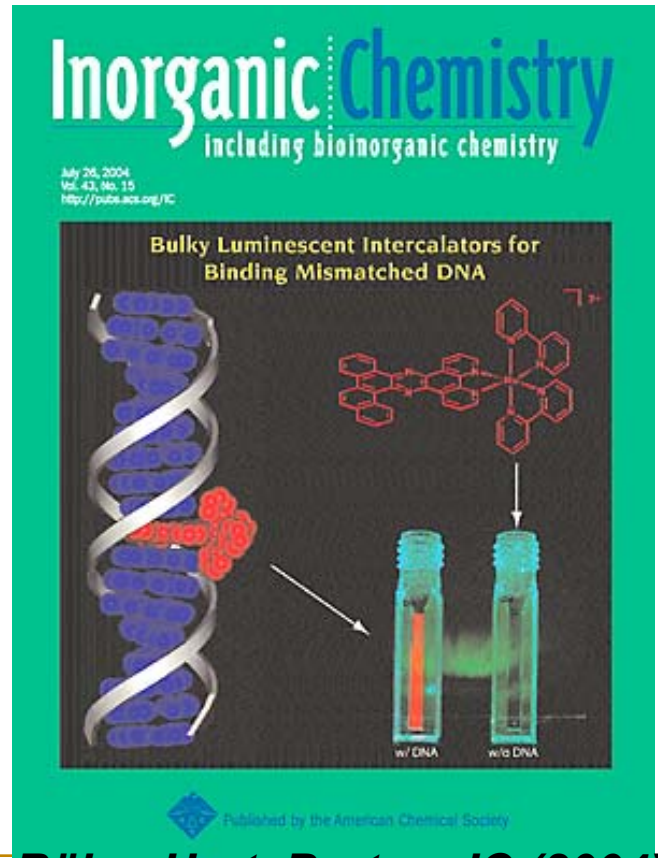
$3d^{10}$ $\qquad$ $3d^{9}$

Tetra-coord. $\qquad$ **Penta-coord.**

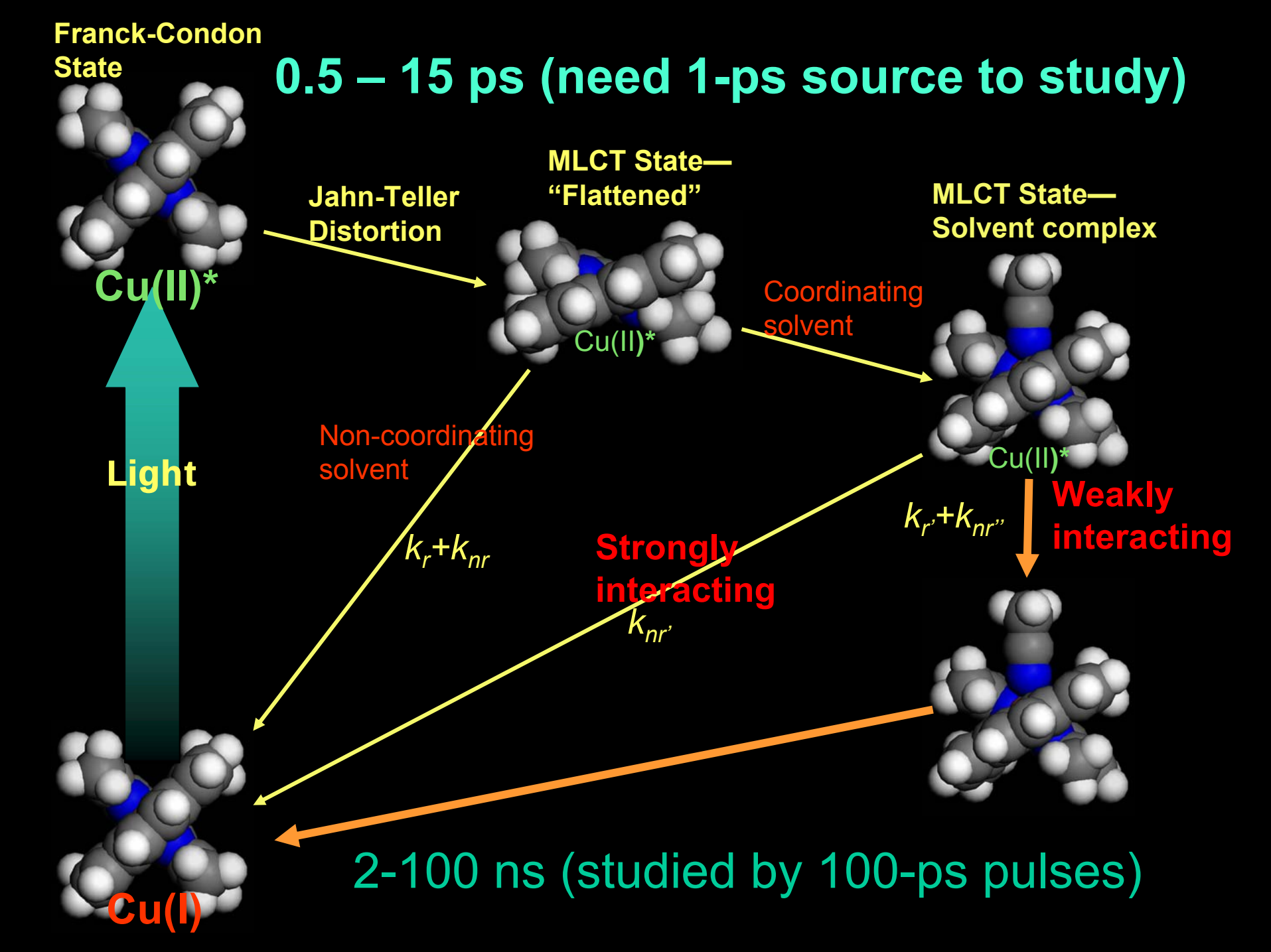




Molecular machines, J.-P. Sauvage, Acc. Chem. Res. 1998

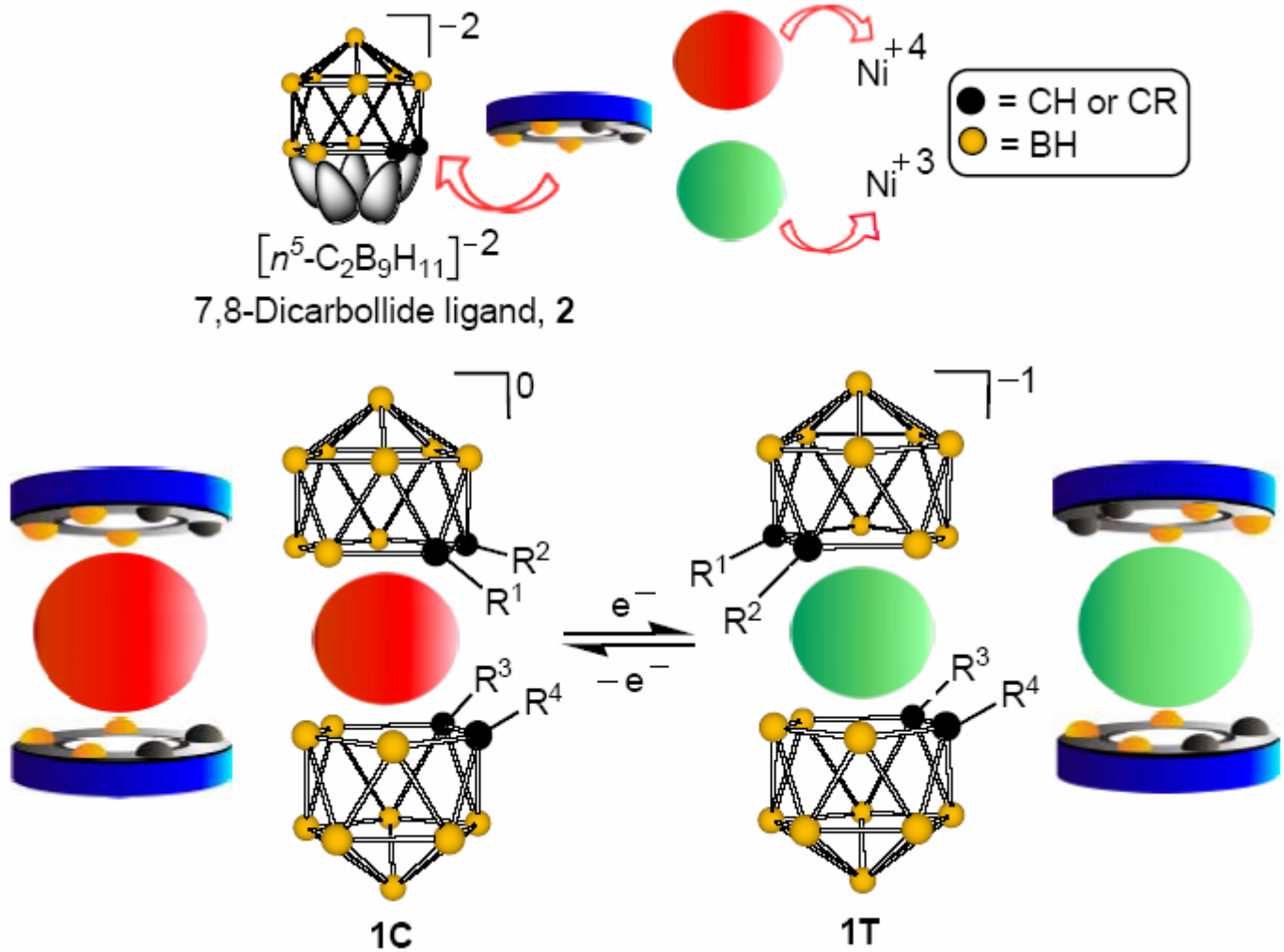


Rüba, Hart, Barton, IC (2004)

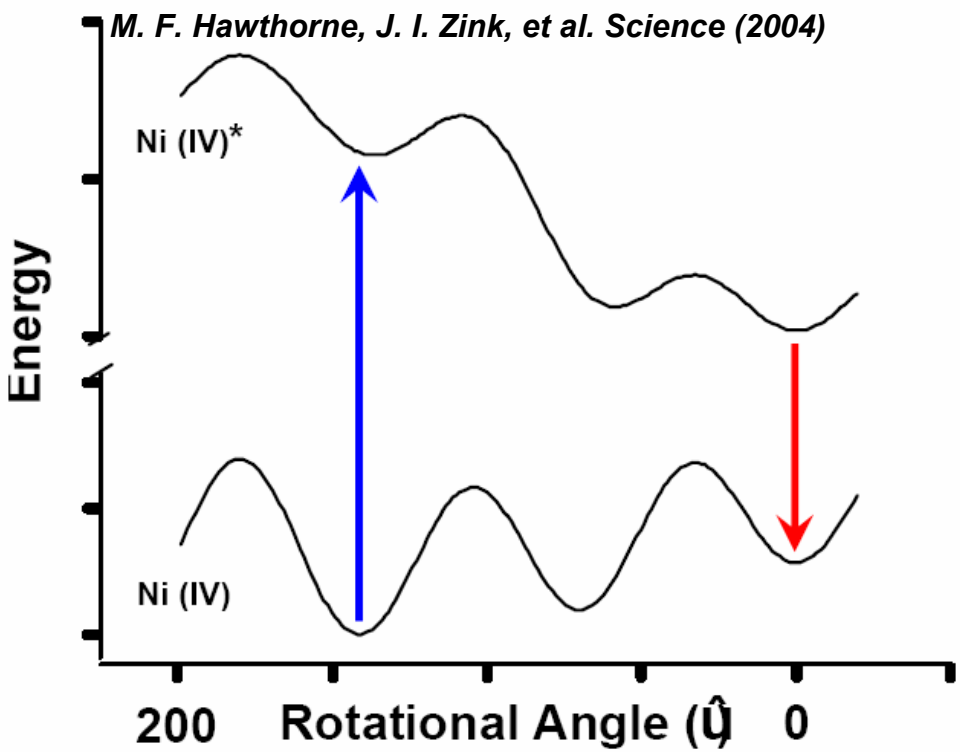

Franck-Condon State
0.5 – 15 ps (need 1-ps source to study)
Cu(II)*
Jahn-Teller Distortion
MLCT State—"Flattened"
Cu(II)*
Coordinating solvent
MLCT State—Solvent complex
Cu(II)*
Light
Non-coordinating solvent
k_r+k_{nr}
Strongly interacting
$k_{nr'}$
$k_{r'}+k_{nr''}$
Weakly interacting
Cu(I)
2-100 ns (studied by 100-ps pulses)

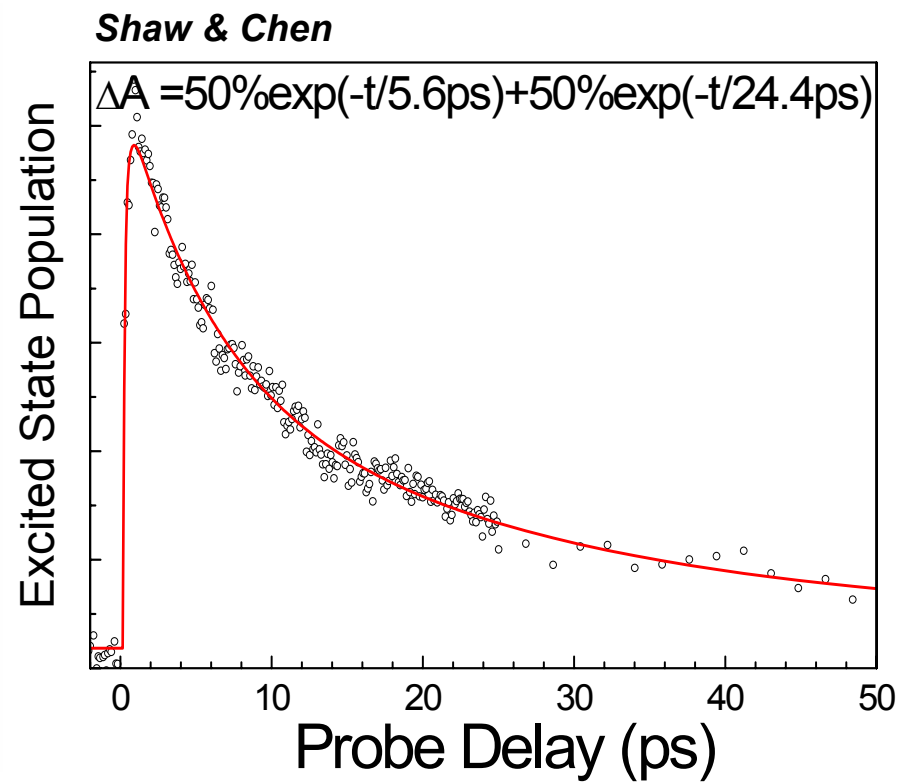
Electrical or Photocontrol of the Rotary Motion of a Metallacarborane

M. F. Hawthorne, J. I. Zink, et al. Science (2004)



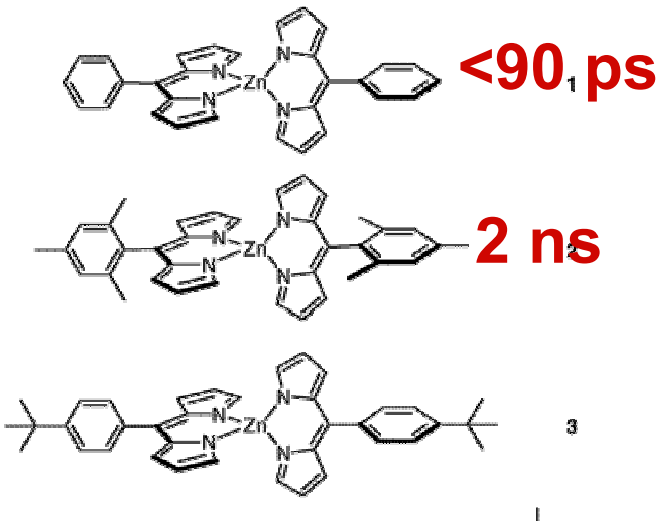
Electrical or Photocontrol of the Rotary Motion of a Metallacarborane



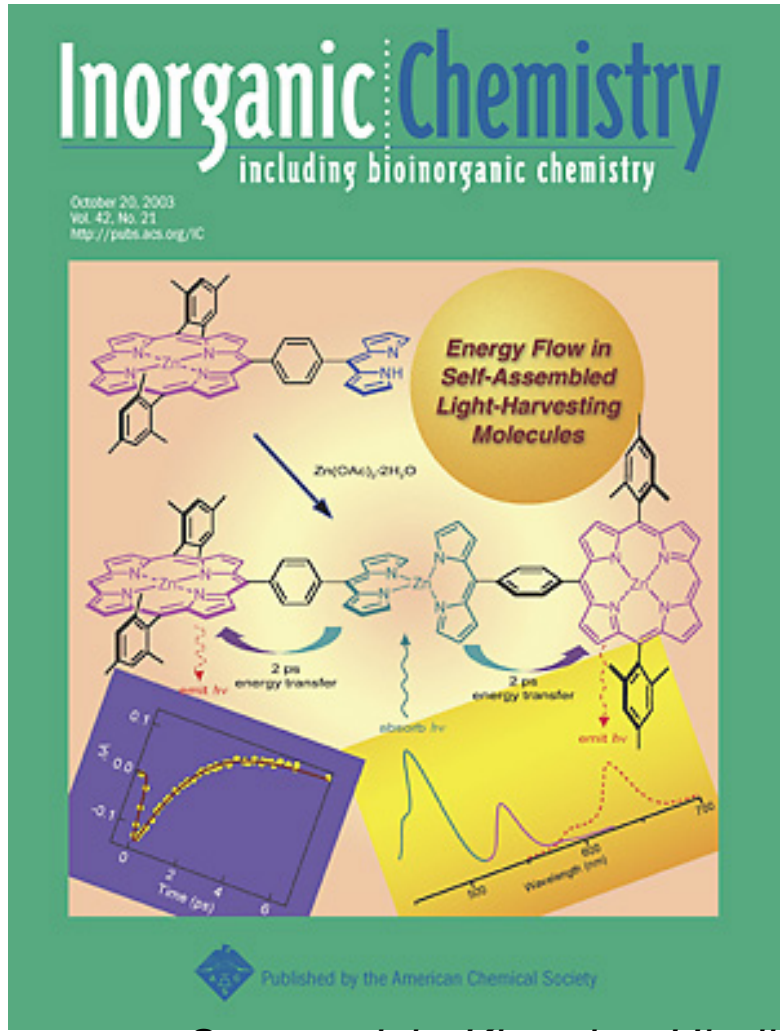


Although the light activated rotation of the motor, the excited state that drives this action has a lifetime 1ps < τ < 100 ps, too short to investigate by current x-ray pulses.

Excited State Structure of Metallo-bisdipyrrin/porphyrin Arrays

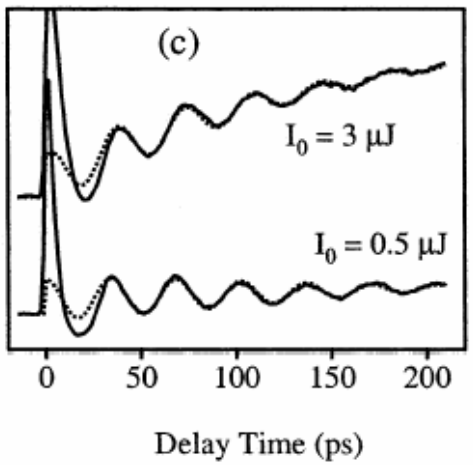


Molecular geometry are critical to their excited state properties. Other transition metal complexes could have even shorter lifetime, i.e. < 10 ps.



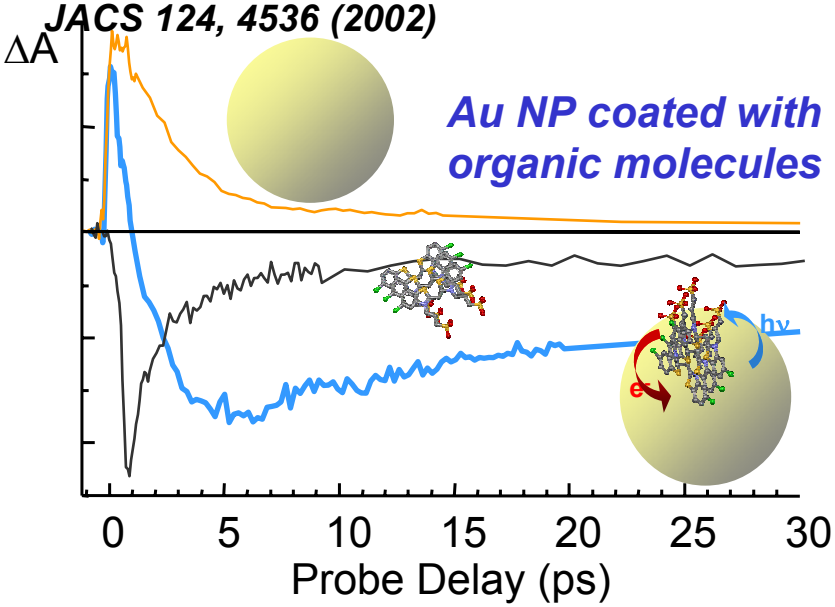
Yu, Muthukumaran, Sazanovich, Kirmaier, Hindin, Diers, Boyle, Bocian, Holten, Lindsey, Inorg. Chem.; 2003; ***42*** *6629 - 6647*

Light Generated Phonons in Metal Nanoparticle Lattices

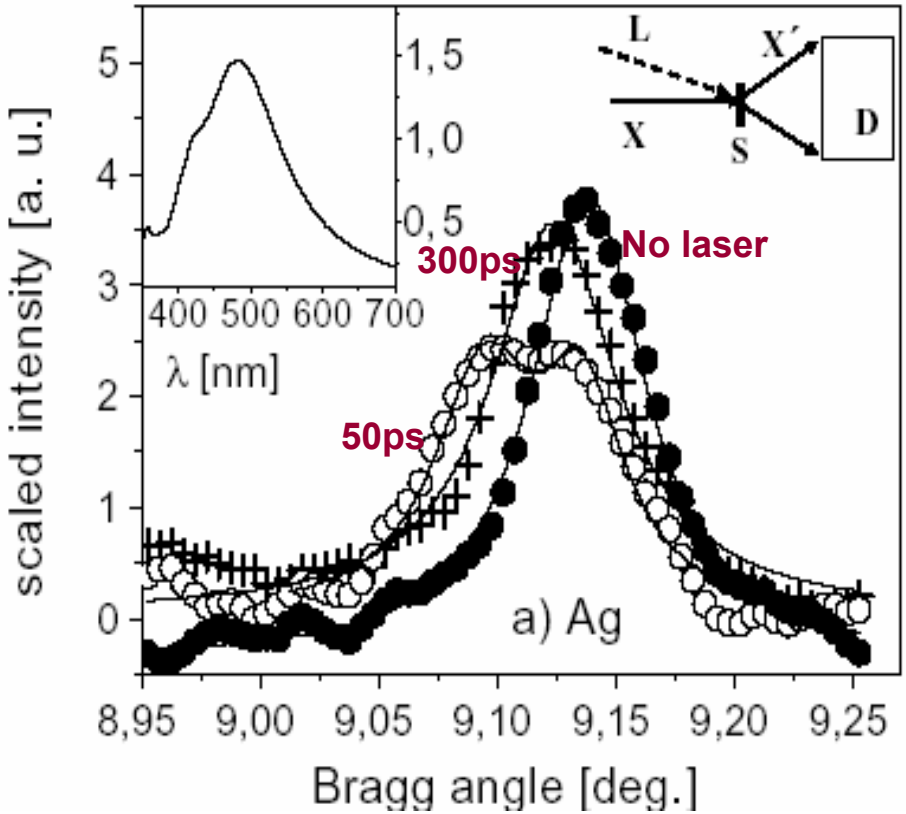


Au NP
G. Hartland
JPCB (2003)

Hranisavljevic, Dimitrijevic, Wurtz, Wiederrecht, JACS 124, 4536 (2002)



Plech et al. Eur. Phys. Lett. (2003)



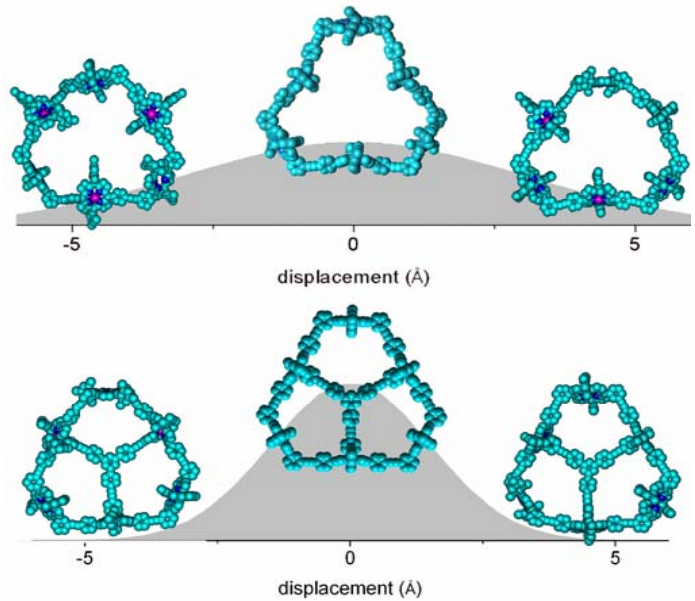
Searching for correlation between transient structures of metal NP and their properties and the influence of light induced phonons to chemical reactivities of molecules adsorbed on the metal NP.

Solution diffraction sensitive measure of molecular conformation, dispersion (dynamics) in solution — D. M. Tiede

Molecular architecture porphyrin wheel

(JACS 2004)

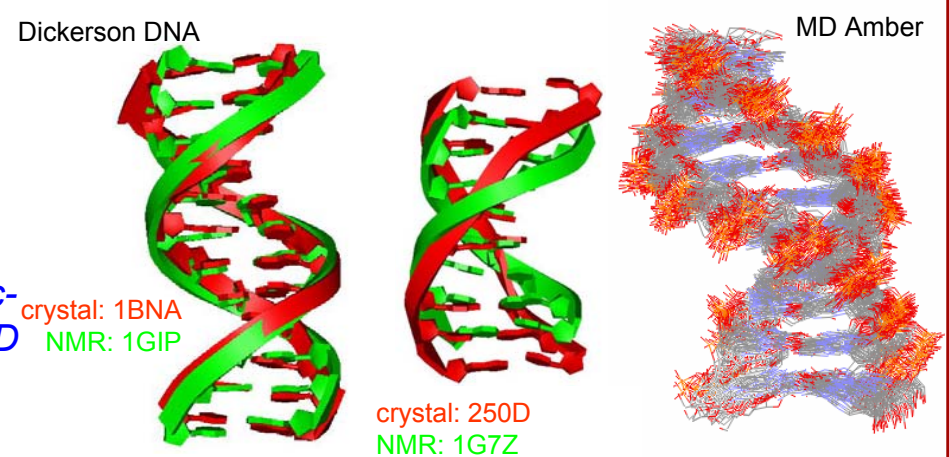
- Cyclic Architecture
- 1.5 Å Shortened "Puckered' Conformation
- Host-Guest Array Expanded 0.6 Å,
- Host Array "Floppy":
  - < 3 Å translational dispersion,
  - Full rotational dispersion
- Host-Guest >2x Smaller Dispersion
- Quantitative test of coordinate models



DNA Solution Structure

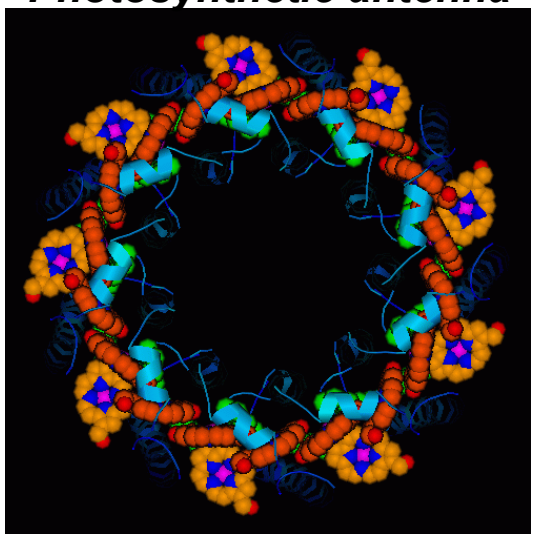
(Molecular wire, ordered model ET matrix)

- Discriminate conflicting crystal and NMR models *(JACS 2004 in press)*
- Discriminate conflicting MD simulations (in preparation)
- *Details solution structure sequence specific- not uniformly predicted by crystal, NMR, MD*

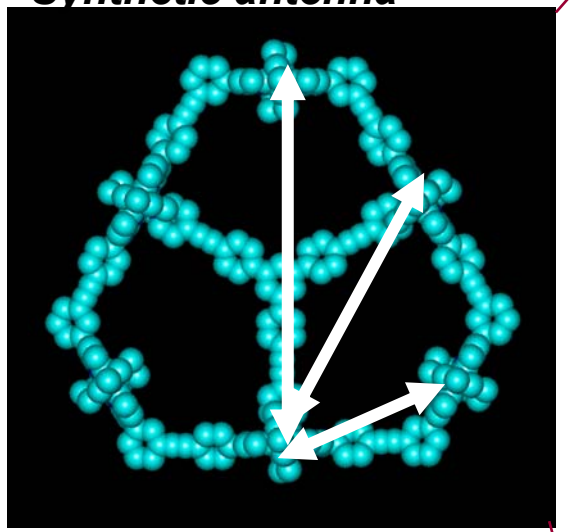


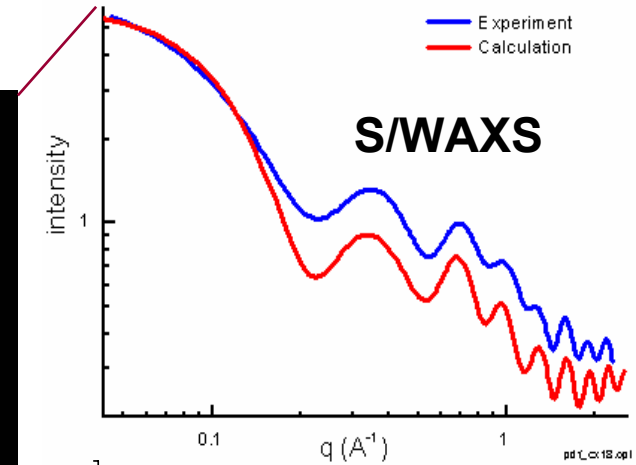
TR-XAS and TR-S/WAXS for Transient Structures on Different Length Scales

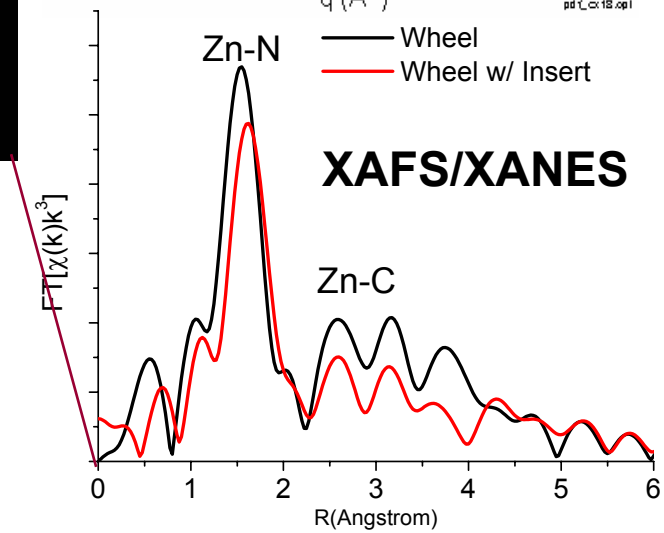
Photosynthetic antenna



Synthetic antenna







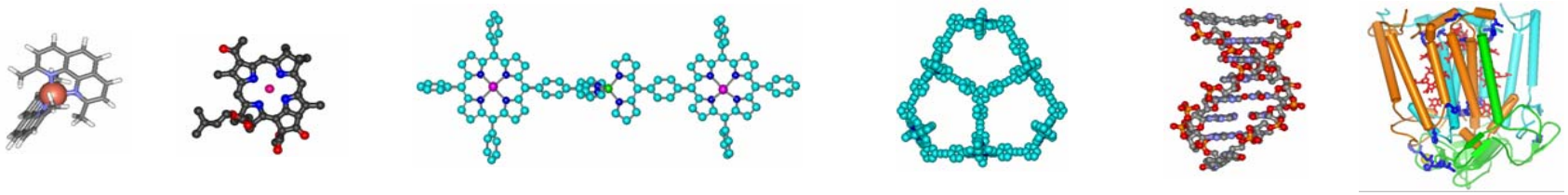
Static and time-resolved X-ray characterization of photoexcited nanoparticles and molecular assemblies ensembles.

WAXS/SAXS – shape, size, solvation and molecular motion, real-time monitoring of self-assembly pathways

XANES – metal oxidation state, coordination environment,

XAFS – bond distances, coordination numbers.

Transient molecular structures on different spatial and time scales



Chemical and biological reactions take place on different time scales from fs to s The molecular structural changes associated with these reactions range from 0.01Å to several Å. Therefore, the molecular movies and snapshots with x-rays should be made with different techniques, such as XAFS, XANES, W/SAXS, and XRD, and taken on different time scales, such as 1 ps to 1s.

Many photochemical processes take place on the time scales from 1-100 ps:

- Internal conversion from upper to lower excited states;
- Excited state relaxation;
- Electron transfer;
- Molecular isomerization;
- Molecular rotation;
- Metal nanoparticle plasmon resonant lattice vibration.

These structural changes are closely related to molecular functions in catalysis, solar energy conversion, molecular devices, hydrogen generation, etc.

1-ps Source Wish List

1. Pulse duration fwhm ~ 1 ps or shorter;
2. Photon flux/pulse at current undulator beamline level;
3. Energy tunability from 4 - 30 keV with energy resolution better or equal to Si 111 monochromator;
4. "Pink" beam capability;
5. Stable spectral and flux in each pulse at current level;
6. Precise synchronization (<<1ps jitter) timing signal installed at all time-domain beamlines which reflects the real timing structure of the x-ray pulses through reliable electronic devices or optical fibers to the experimental hutches;
7. Beam size on the order of 0.1 mm diameter or smaller;
8. X-ray shutter installed at each time-domain beamline capable of extracting single pulse from one or more operating modes, i.e. 24-bunch mode or hybrid mode;
9. Compatible fs or ps laser systems;
10. Detector development for spectroscopy and diffraction/scattering to accommodate time-domain experiments on time scales from 1 ps to 1μs, (i.e. multilayer Si detector array, Si drift detector, CCD, concentric metal wire detector, etc).
11. Coordinate among BES beamlines by requesting time-domain users to submit their experimental needs in terms of different parameter ranges. Such a survey will provide guidance for regrouping users into different beamlines in the future.
12. Form a committee or group of user representatives to communicate the scientific needs to the APS and to see the improvements and plans being implemented.

Probing Ultrafast Structural Reorganizations in Photo
Reactions: from Molecules to Nanoparticles

Personnel

David J. Gosztola[1*], Project coordinator,
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LOI for LCLS from Chemistry Division and Partners

- **Molecular Motions and Transition State Structures in Chemical Reactions**
- **Real Time Structural Dynamics in Size-Selected Clusters**
- **Semiconductor Nanostructures**
- **Coherent Control**

1-ps x-ray source can be used for <u>some but not all</u> proposed experiments and serve as a test-bed for LCLS experiments. The coherence, pulse duration, and pulse flux of LCLS are its characteristics that exceed other sources.

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